

REPORT DOCUMENTATION PAGE

AD-A207 185

TIC
ECTE

2b. DECLASSIFICATION/DOWNGRADING SCHEDULE 26 APR 1989

4. PERFORMING ORGANIZATION REPORT NUMBER(S)

D 28

1b. RESTRICTIVE MARKINGS

3. DISTRIBUTION/AVAILABILITY OF REPORT

Approved for public release;
distribution is unlimited.

5. MONITORING ORGANIZATION REPORT NUMBER(S)

AFOSR-TR-89-0473

6a. NAME OF PERFORMING ORGANIZATION

Boston University

6b. OFFICE SYMBOL
(If applicable)

7a. NAME OF MONITORING ORGANIZATION

AFOSR/NP

6c. ADDRESS (City, State, and ZIP Code)

Boston, MA 02215

7b. ADDRESS (City, State, and ZIP Code)

Building 410, Bolling AFB DC
20332-64488a. NAME OF FUNDING/SPONSORING
ORGANIZATION

AFOSR

8b. OFFICE SYMBOL
(If applicable)

NP

9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER

AFOSR-84-0261

8c. ADDRESS (City, State, and ZIP Code)

Building 410, Bolling AFB DC
20332-6448

10. SOURCE OF FUNDING NUMBERS

PROGRAM
ELEMENT NO.

61102F

PROJECT
NO.

2301

TASK
NO.

A4

WORK UNIT
ACCESSION NO.

11. TITLE (Include Security Classification)

(U) FLUORESCENCE PROBES OF SPECTROSCOPIC & DYNAMICAL ASPECTS OF MOLECULAR PHOTOIONIZATION

12. PERSONAL AUTHOR(S)

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13a. TYPE OF REPORT
FINAL

13b. TIME COVERED

FROM 1 Jul 84 TO 30 Jun 88

14. DATE OF REPORT (Year, Month, Day)

November 1988

15. PAGE COUNT

4

16. SUPPLEMENTARY NOTATION

17. COSATI CODES

FIELD	GROUP	SUB-GROUP
	20.08	

18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

Studies have been made of vibrationally resolved aspects of shape resonant excitation in the photoionization of N(2)O. This experiment was performed by generating dispersed fluorescence spectra from electronically excited photoions. These results are the first vibrationally resolved results on a polyatomic shape resonance. In vibrationally resolved measurements, different internuclear configurations are probed by sampling alternative vibrational levels of the ion. As a result, the continuum electron behavior can be mapped out most clearly, and the qualitative aspects of the electron ejection can be understood clearly. A central motivation for studying polyatomic shape resonances is that alternative vibrational modes may be explored, revealing facets that are nonexistent for diatomic systems, which are the only systems that have been characterized previously.

20. DISTRIBUTION/AVAILABILITY OF ABSTRACT

X ☐ UNCLASSIFIED/UNLIMITED X ☐ SAME AS RPT ☐ DTIC USERS

21. ABSTRACT SECURITY CLASSIFICATION

UNCLASSIFIED

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22c. OFFICE SYMBOL

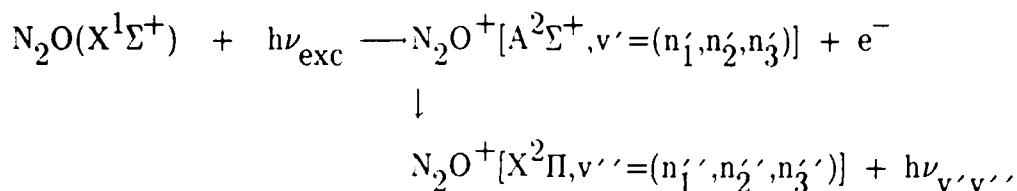
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FINAL TECHNICAL REPORT

Vibrational branching ratios serve as sensitive experimental probes of resonance phenomena in molecular photoionization.¹ In the absence of resonant excitation, the Franck-Condon approximation holds and vibrational branching ratios are independent of photon energy. Conversely, deviation from Franck-Condon behavior is an indicator of resonance excitation. We have studied vibrationally resolved aspects of shape resonant excitation in the photoionization of N_2O . This experiment is performed by generating dispersed fluorescence spectra from electronically excited photoions. These results by our group are the first vibrationally resolved results on a polyatomic shape resonance, and they illustrate the basic ideas of the project clearly. The reason that vibrationally resolved measurements are important is that different internuclear configurations are probed by sampling alternative vibrational levels of the ion. As a result, the continuum electron behavior can be mapped out most clearly, and the qualitative aspects of the electron ejection can be understood clearly. This is not surprising, in that measurements that probe molecular aspects of the process, such as vibration, are most intimately related to molecular insights of the scattering process. A central motivation for studying polyatomic shape resonances is that alternative vibrational modes may be explored, revealing facets that are nonexistent for diatomic systems, which are the only systems that have been characterized previously.

Electronically excited ions are produced via synchrotron radiation excitation and we detect the ionic fluorescence to provide relative cross section information.² Specifically, the relative production rates for alternative vibrational levels of the A state N_2O ion are determined using dispersed fluorescence detection.

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The three vibrational indices denote the number of quanta for the symmetric stretch, bend, and antisymmetric stretching modes, respectively. The fluorescence intensity originating from level v' is a measure of the rate of production of that level, i.e., its partial photoionization cross section, $\sigma_{v'}$. By measuring the fluorescence intensity for a particular transition as a function of excitation energy, we obtain a constant ionic state (CIS) spectrum.²⁻⁴ By sampling alternative vibrational levels of the ion as a function of the excitation energy, these studies illuminate the interplay between the electronic and nuclear degrees of freedom that determine the molecular photoionization dynamics. The ratio of CIS scans can reveal the presence of resonant excitation.

The attached figure shows such ratio curves, and are quite revealing. The ratio of the (0,0,1) and (0,0,0) curves is essentially constant over the excitation energy range studied, while the ratio of the (1,0,0) versus the (0,0,0) curves is extremely nonconstant (i.e., non-Franck-Condon). This indicates that the resonance affects the (1,0,0) cross section differently than either the (0,0,1) or (0,0,0) vibrational levels. A rather simple interpretation can be ascribed to this behavior, namely, the barrier that traps the photoelectron extends beyond the periphery of the ion. As a result, the (0,0,0) and (0,0,1) curves appear quite similar because the vibrational motion for either of these levels does not affect the molecular volume appreciably, or therefore, the barrier to photoelectron ejection. On the other hand, the (1,0,0) vibration of the ion results in a breathing motion of the nuclei, and this might affect the barrier to photoelectron ejection. As a result, the partial photoionization cross-section curve for this level behaves differently than either of the other vibrational cross-section curves. Further studies in this vein are planned. In

particular, larger polyatomic systems are of interest, so that electron-optical effects can be studied where more degrees of freedom (i.e., more vibrational modes) are accessible. The strategy for studying such systems is identical to that for the case presented here, and more detailed insights into fundamental molecular scattering phenomena become possible.

References

1. A recent review with several examples is: J.L. Dehmer, D. Dill, and A.C. Parr, in *Photophysics and Photochemistry in the Vacuum Ultraviolet*, ed. S. McGlynn, G. Findley, and R. Huebner (Reidel, Dordrecht, 1985)
2. E.D. Poliakoff, M.-H. Ho, G.E. Leroi, and M.G. White, *J. Chem. Phys.* **84**, 4779 (1986)
3. T.A. Carlson, W.A. Svensson, M.O. Krause, T.A. Whitley, and F.A. Grimm, *J. Chem. Phys.* **83**, 3738 (1985)
4. E.W. Plummer, T. Gustafson, W. Gudat, and D.E. Eastman, *Phys. Rev. A* **15**, 2339 (1977)

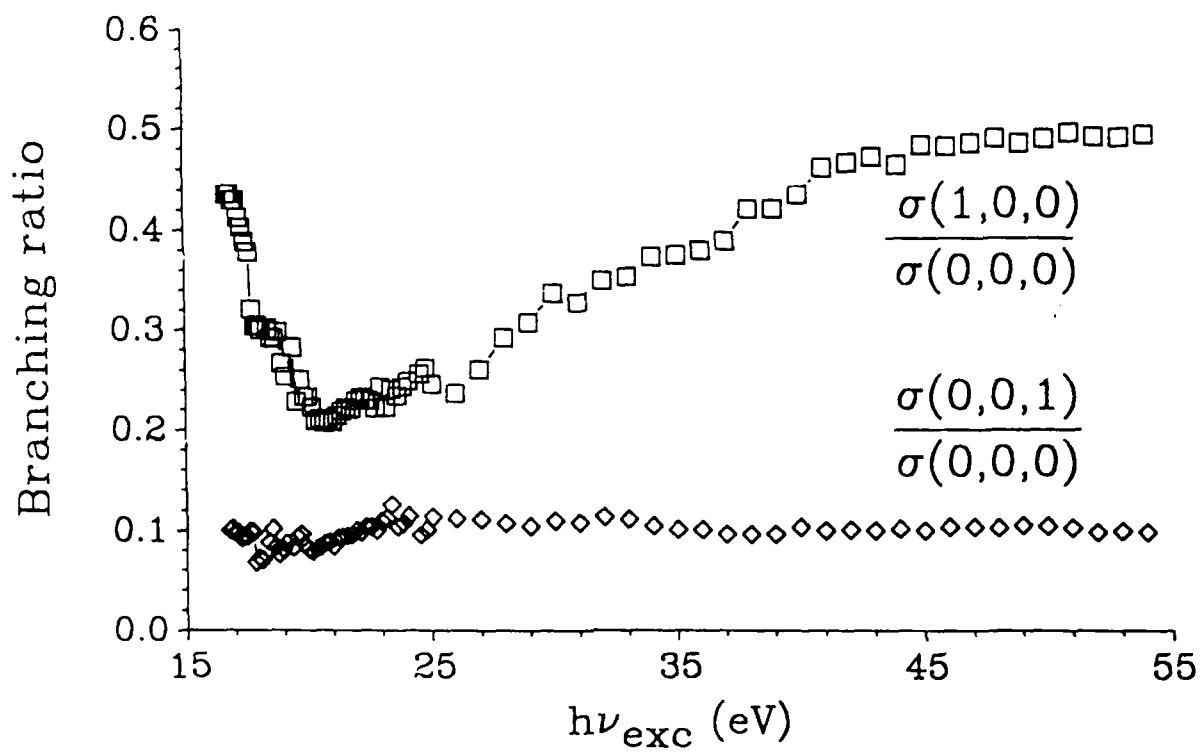


Figure caption: Vibrational branching ratio curves for the $\text{N}_2\text{O}^+(\text{A}^2\Sigma^+)$ state, $\sigma(1,0,0)/\sigma(0,0,0)$ and $\sigma(0,0,1)/\sigma(0,0,0)$.